PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C01B 17/00, C01F 11/46

A1

(11) International Publication Number: WO 93/01125

(43) International Publication Date: 21 January 1993 (21.01.93)

(21) International Application Number: PCT/US92/05600

(22) International Filing Date: 2 July 1992 (02.07.92)

(30) Priority data:
725,505 3 July 1991 (03.07.91) US

(71) Applicant: RADIAN CORPORATION [US/US]; 8501 Mo-Pac Boulevard, P.O. Box 201088, Austin, TX 78720-4797 (US).

(72) Inventors: COLLEY, James, David ; 12307 Log Cabin Lane, Louisville, Kentucky 40233 (US). BURKE, John, M. ; 3741 Terramar Court, Chamblee, GA 30341 (US). LOWELL, Philip, S. ; 3308 Rivercrest Drive, Austin, TX 78746 (US).

(74) Agent: KLAUBER, Stefan, J.; Klauber & Jackson, Continental Plaza, 411 Hackensack Avenue, Hackensack, NJ 07601 (US).

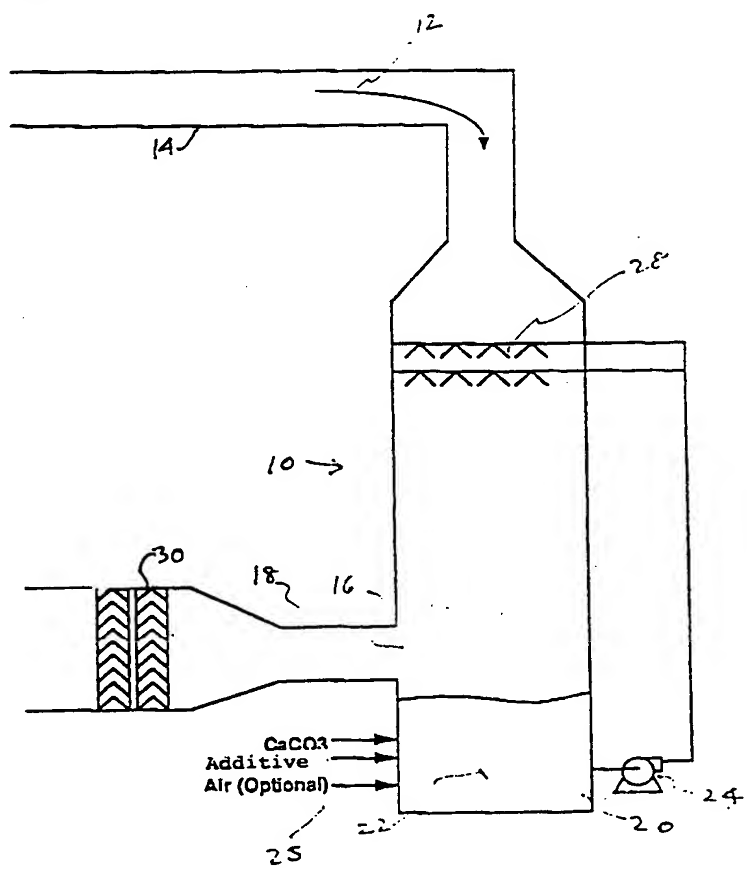
(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).

Published
With international search report.

(54) Title: COCURRENT SCRUBBER METHOD AND SYSTEM

(57) Abstract

A method for desulfurizing flue gases in an absorber tower while maintaining a differential pressure across the absorber inlet-outlet of zero or less. An absorber tower (10) is used which is devoid of packing, and which has a flue gas inlet (14) at the upper end thereof and a treated flue gas outlet (18) toward the bottom end. An aqueous slurry is sprayed into an upper region (28) of the tower which includes (1) an absorbent for the sulfur-containing gases in said flue gases, and (2) one or more additional compositions which enhance the absorption of said sulfur-containing gases by scrubbing with said slurry. The sprayed slurry thereby mixes with the flue gases and descends cocurrently in the tower. The treated gases are separated from the slurry and flowed to the outlet of the tower.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland			SN	Senegal
CI	Côte d'Ivoire	KR	Republic of Korea	SU	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
CS	Czechoslovakia	LK	Sri Lanka	TG	Togo
DE	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		
ES	Spain	MG	Madagascar		

COCURRENT SCRUBBER METHOD AND SYSTEM

Field of the Invention

This invention relates generally to processes for desulfurization of flue gases, and more specifically relates to an improved scrubber method which enables effective use of an open spray tower to permit operation of the absorber with a differential inlet to outlet pressure of zero or less.

REFERENCE TO DISCLOSURE DOCUMENT

This invention is related to our Disclosure Document No. 249993, filed April 5, 1990, which is hereby incorporated by reference.

BACKGROUND OF THE INVENTION

Air pollution is a very serious and urgent international problem. The sources of air pollution are primarily the products of combustion and are numerous and widespread. Many of the air pollutants are in the form of sulfur-bearing flue gases discharged by fossil-fuel-burning electrical power generating plants or other industries. While the precise impact of these pollutants on the environment is still a subject of some speculation, evidence continues to mount which demonstrates serious adverse effects. Yet, under foreseeable circumstances, it will be necessary to burn more and more fuel to meet the demands of a rapidly growing population requiring for each person evermore heating comfort and power, and the fuel which will generally be used will not contain much less sulfur, but will likely contain more sulfur.

Thus, sulfur oxides, principally present as sulfur dioxide, are found in the waste gases discharged from many metal refining and chemical plants, and in the flue gases from power plants generating electricity by the combustion of fossil fuels. In addition, sulfur-

containing gases, notably sulfur dioxide, may be formed in the partial combustion or gasification of sulfur-containing fuels, such as coal or petroleum residues. The control of air pollution resulting from the discharge of sulfur dioxide into the atmosphere has thus become increasingly urgent.

The most common flue gas desulfurization (FGD) process is known as the "wet process". In that process the sulfur dioxide-containing flue gas is scrubbed with a slurry containing, e.g. limestone. The scrubbing takes place, for example, in an absorption tower in which the gas flow is countercurrent to and in intimate contact with a stream i.e. a spray of slurry. Most commonly the slurry is made to flow over packing or trays. The spent slurry product of this FGD process contains both calcium sulfite and calcium sulfate. It has been found to be advantageous to convert the calcium sulfite in the product to calcium sulfate by bubbling air or other oxygen-containing gas through the slurry.

SUMMARY OF INVENTION

Briefly, and in accordance with the present invention, additives which enhance the SO_2 removal efficiency of lime or limestone scrubbers are combined with a cocurrent absorber design which is essentially an open spray tower. This permits operation of the absorber with a differential pressure of zero or less.

Existing cocurrent absorber designs require packing to achieve reasonable SO_2 removal efficiencies. The presence of this packing results in a positive differential pressure inlet-to-outlet (i.e., a net pressure drop) for the treated flue gas across the absorber which requires a booster fan or booster fan modification to overcome. Other absorber designs also result in a significant flue gas pressure drop and thus have the same booster fan

requirement. In accordance with the present invention it has been found possible to even achieve a pressure rise in a cocurrent absorber if no packing material is included.

Existing cocurrent absorber designs include packing to provide adequate SO_2 removal efficiency performance at reasonable slurry recirculation rates. However, it is possible to eliminate the requirement for packing material if additives such as formic, adipic, glutaric and/or succinic and/or a mixed dibasic acid (DBA) or their salts; or the oxides, hydroxides, carbonates, or sulfates of sodium or magnesium are used to enhance the SO_2 removal performance of the absorber. With the packing removed, gas flowing through the absorber will be accelerated by the slurry spray and the gas pressure can actually rise across the absorber (i.e., the absorber will have a negative pressure drop). Thus, it is feasible to install a cocurrent absorber which uses SO_2 removal enhancement additives without the addition of a special booster fan or with minimum modification of an existing fan. A design such as this is especially useful for FGD retrofit applications, eliminating the need for expensive fan modification.

Another advantage of the cocurrent absorber design in retrofit applications is that cocurrent absorbers can be operated at higher gas velocities than countercurrent absorber designs. This advantage has two related benefits. First, the absorber cross-section can be smaller for cocurrent absorbers than for countercurrent absorbers. Thus, less space is required, which can be especially important in retrofit applications where available space is at a premium. Secondly, the "turn-up" ratio for cocurrent absorbers is better than for countercurrent absorbers. That is to say, the gas flow rate can be increased with less deleterious impact on performance for cocurrent absorbers than for

countercurrent absorbers. Thus, it is easier to take a scrubber module "out of service" and treat all of the gas in the remaining on-line absorbers.

The separate use of cocurrent absorber design and the use of SO_2 removal (i.e. absorber) enhancement additives are per se well-known technologies. The combined use of these two concepts, however, has been found to function synergistically to provide unexpected benefits, including the ability to operate the FGD absorber with a gas-side pressure rise and the reduced cross-sectional area which can be achieved using a cocurrent absorber. These benefits are of particular value to utilities faced with the retrofit of FGD systems.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIGURE 1 is a schematic cross-sectional view of a cocurrent scrubber system in accordance with the invention;

FIGURE 2 is similar to Figure 1, but illustrates a two module operation; and

FIGURE 3 is similar to Figure 2, but illustrates the manner in which the invention facilitates gas flow turn-up where a module is taken out of service.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In Figure 1 a cross-section view appears of a cocurrent scrubber system embodying the principles of the invention. There is shown a flue gas scrubbing absorber tower 10 to which flue gases 12 are provided by the conduit 14. The flue gases may be considered as resulting from a typical combustion process which as a

result of the fuel utilized includes substantial sulfur-containing gases, most notably sulfur dioxide, and it is desired to remove these gases by the scrubbing action in the tower 10. It is seen that the conduit 14 enters the upper reaches or top of tower 10, and that the gases then descend, i.e. proceed in a downward direction through tower 10 and exit by an outlet 16 into outlet conduit 18. The gases leaving can be regarded as being treated gases, i.e. they are substantially purified of the sulfur-containing components, notably SO_2. At the bottom of the tower 10 is a sump 20, which in turn defines a reservoir 22 for an aqueous slurry. The slurry includes a suspension of lime or limestone, i.e. calcium carbonate, as well as calcium sulfate which has formed from the scrubbing step, and in addition includes one or more agents or compositions which enhance the absorption of the sulfur-containing components such as SO_2 during the scrubbing action in tower 10. The slurry at sump 20 typically includes 10 to 15% by weight solids. The absorption enhancing compositions are well-known in the art, and may be selected from one or more members of the group consisting of formic acid, adipic acid, glutaric acid, succinic acid, or the salts of any of the foregoing acids; as well as the oxides, hydroxides, carbonates or sulfates or sodium or magnesium. A preferred additive is so-called "diabsic acid" which is a mixture of adipic, glutaric and succinic acids - one such product being commercially available from the Monsanto Company. The said additives are typically present as from 1,000 to 5,000 ppm of the scrubbing liquor (i.e. the liquid phase of the slurry). The mixed slurry in sump 20 is pumped by pump 24 to the upper regions of the tower 10, where the slurry is then sprayed by a spraying means 28 mounted at the upper regions of the tower.

It is thus seen in accordance with the invention that the sprayed slurry including the lime or limestone absorbent and the absorption enhancing agents is mixed with the

flue gases in the upper regions of tower 10 and then descends cocurrently in same. The spent or partially spent slurry collects at the bottom of the tower in the reservoir 24 at sump 22 and the scrubbed gases proceed via outlet 16 and conduit 18 through a standard demister 30 to an exit stack or to electrostatic precipitators or the like which may further purify the gases. The sump 20 may optionally be provided with means to provide forced oxidation in same as shown at 25. Specifically, an air injection means may be positioned within the body of reservoir 22, preferably at the bottom of same, as for example in the form of a sparger into which air is injected under pressure as by means of a pump. Certain aspects of the advantages of forced oxidation are discussed in U.S. Patent No. 4,876,076.

Typical L/G (liquid-to-gas) ratios in the tower 10 may be in the range of from 60 to 130 gal/1,000 ft^3. In accordance with the present invention, it is seen that the tower 10 is devoid of packing media which are normally required in the prior art, particularly in countercurrent scrubbing operations. Thus tower 10 is essentially an open spray tower. This assures that the pressure drop between inlet and outlet in the tower is minimal, and actually is in practice found to be of zero or even of negative value.

By reference to Figures 2 and 3, one of principal advantages of the present arrangement may be seen. More specifically in Figure 2, a two module operation is set forth in which two towers 32 and 34 appear which are substantially as described in connection with Figure 1. The gas outlets 36 and 38 from each of these towers are provided to a common stack 40. Representatively, as shown in Figure 2, a gas velocity of 15 feet per second may be assumed in each of the two modules. Referring to Figure 3, it is assumed that the module schematically depicted on the left, i.e. module 32, is inactivated as

by being taken off line for maintenance or other purposes. In accordance with the present invention, the gas velocity in the remaining on line module 34 may be readily increased to a velocity as shown, of 30 feet per second with minimal effects on efficiency or pressure drop, by virtue of the fact that said towers are devoid of packing, which normally would render this type of vast increase in gas flow turn-up extremely difficult or impossible to achieve.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

WHAT IS CLAIMED IS:

1. A method for desulfurizing flue gases in an absorber tower while maintaining a differential pressure across the absorber inlet-outlet of zero or less; comprising:

providing an absorber tower which is devoid of packing, and having a flue gas inlet at the upper end thereof and a treated flue gas outlet toward the bottom end; and spraying into an upper region of said tower an aqueous slurry which includes (1) an absorbent for the sulfur-containing gases in said flue gases, and (2) one or more additional compositions which enhance the absorption of said sulfur-containing gases by scrubbing with said slurry; said sprayed slurry thereby mixing with said flue gases and descending cocurrently in said tower; and separating the treated gases from said slurry and flowing said treated gases to said outlet of said tower.

2. A method in accordance with claim 1, wherein said absorbent comprises lime or limestone.

3. A method in accordance with claim 2, wherein said composition for enhancing adsorption of said sulfur-containing gases, is selected from one or more members of the group consisting of formic, adipic, glutaric, succinic acids or their salts, and the oxides, hydroxides, carbonates or sulfates of sodium or magnesium.

4. A method in accordance with claim 3, wherein said absorbing enhancement composition comprises a mixture of adipic, glutaric and succinic acids.

5. A method in accordance with claim 1, wherein said absorber tower includes a sump at the bottom thereof, which defines a reservoir for said slurry, said slurry being pumped to the upper region of said tower for

spraying, and being collected at said sump following its descent in said tower.

6. A method in accordance with claim 5, wherein said enhancement composition is added to said slurry at said sump.

7. A method in accordance with claim 5, further including providing forced oxidation at said sump by bubbling air into same.

8. A method in accordance with claim 5, wherein the separated treated flue gases are passed from said tower outlet to a demister.

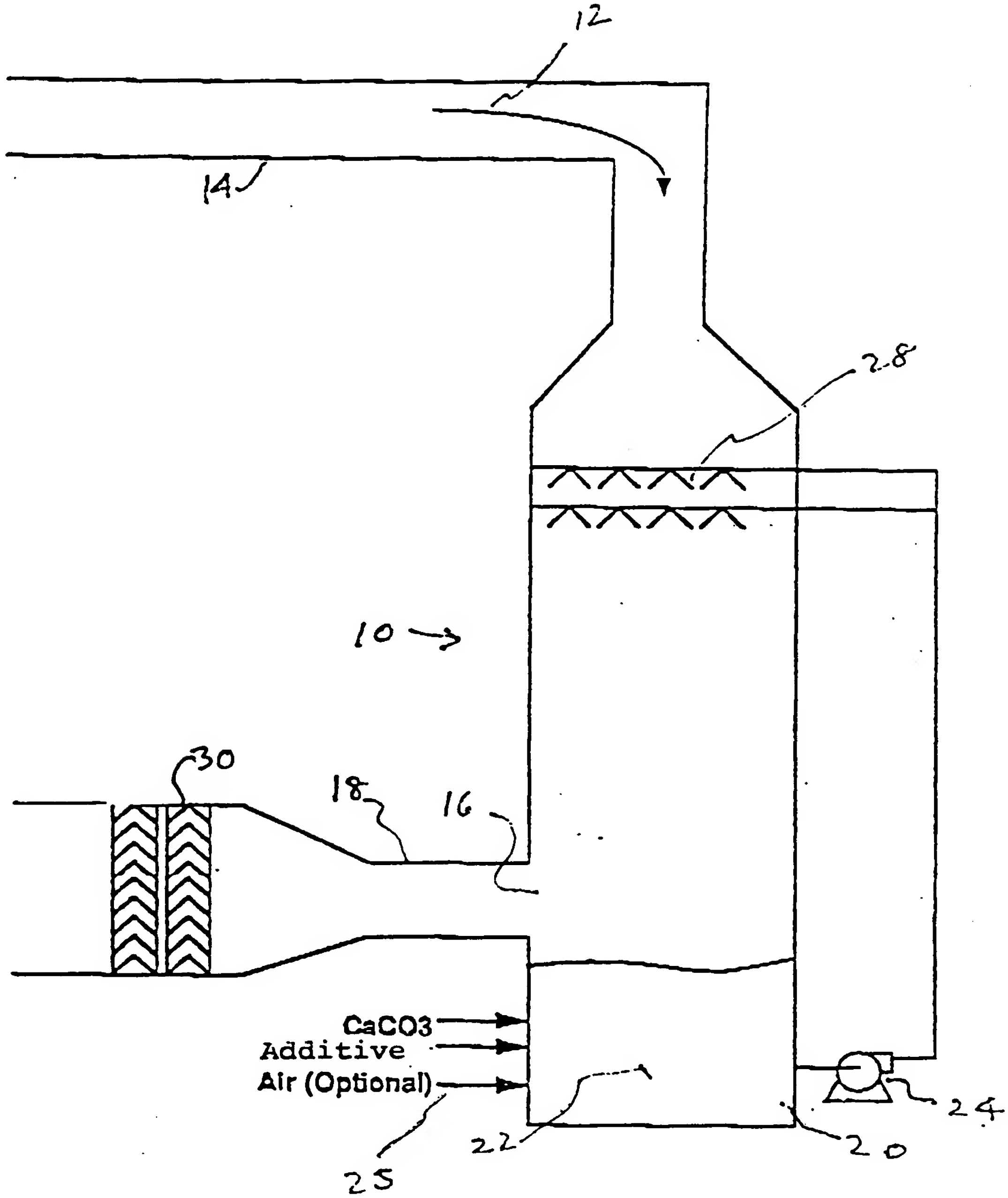


FIGURE 1

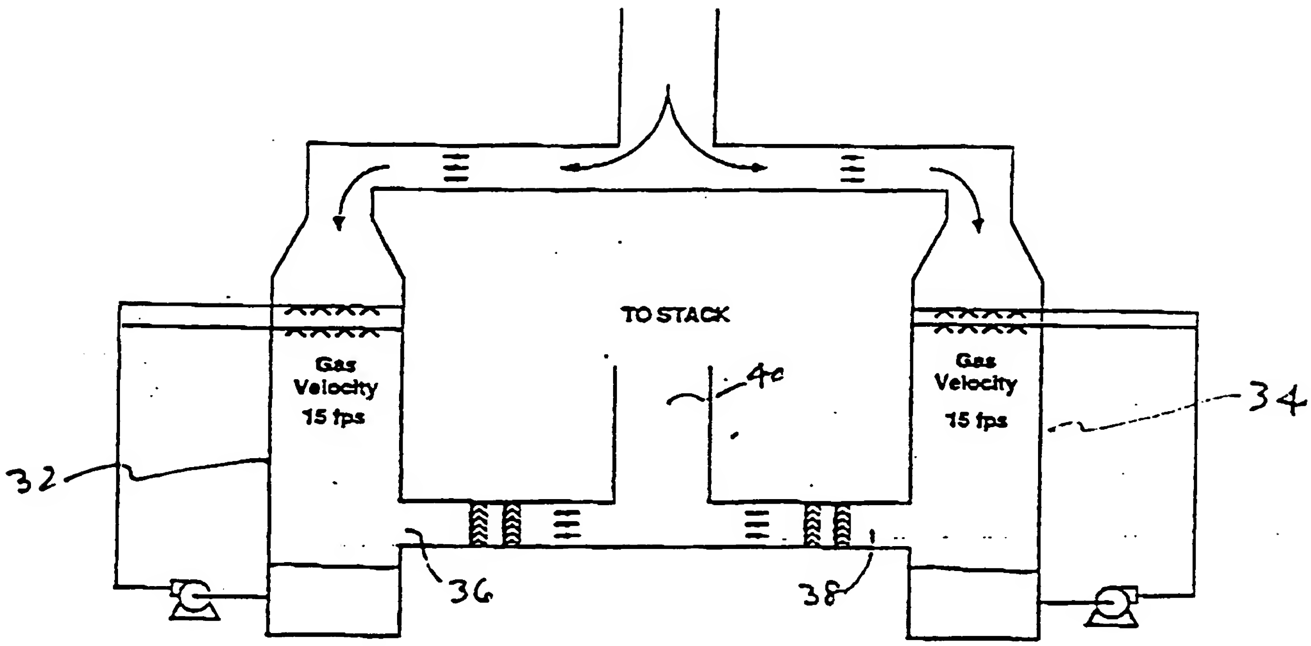


FIGURE 2

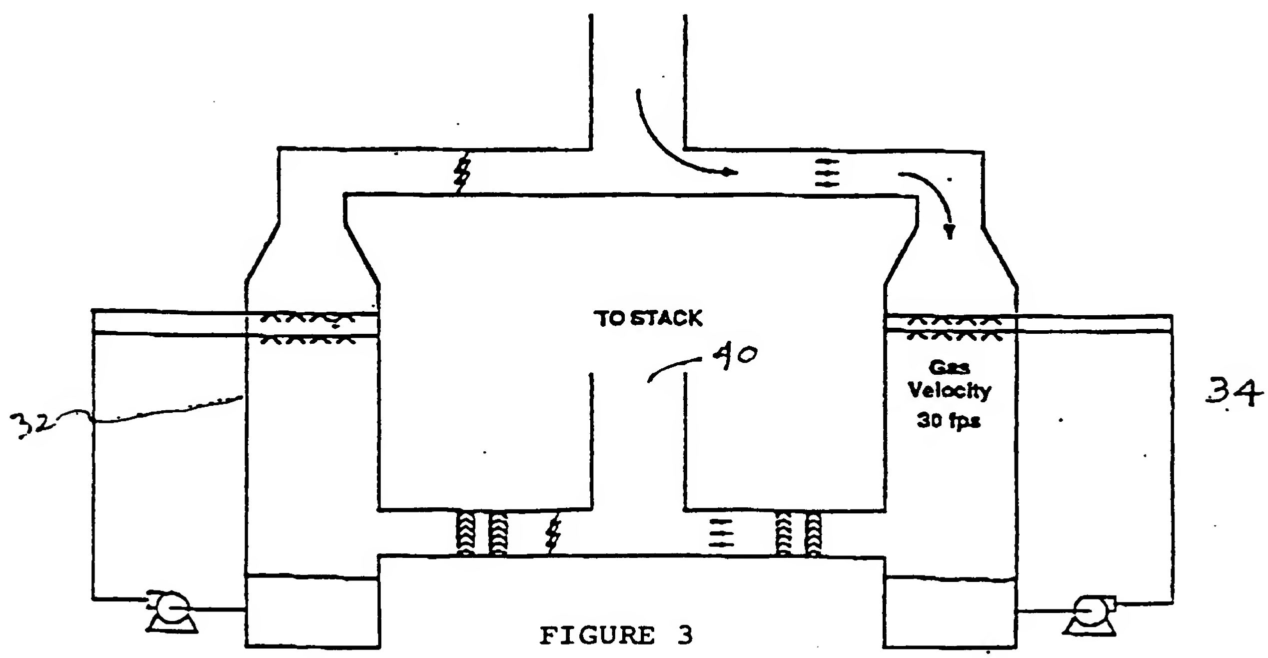


FIGURE 3

INTERNATI AL SEARCH REPORT

International application No.
PCT/US92/05600

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01B 17/00 C01F 11/46
US CL :423/232, 233, 242A AND 555
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : NONE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,891,195 (LIN) 02 January 1990, see col. 2, lines 10-35.	1,3,4
Y	US,A, 4,366,132 (HOLTER et al) 28 December 1982, see col. 3, lines 23-28 and figure 1.	7
Y	US,A, 3,904,742 (AKIMOTO) 09 September 1975, see col. 2, lines 63-68 and col. 4, lines 47-51.	3
Y	US,A, 3,775,532 (SHAH) 27 November 1973, see col. 3, lines 41-49; col. 6, lines 36-57 and figure 1.	1,2,5,6,8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 AUGUST 1992	21 SEP 1992

Name and mailing address of the ISA/ US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Ngoc-Ho Nguyen TIMOTHY C. VANOY NGOC-HO INTERNATIONAL DIVISION
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-2540

PCT/US92/05600
03 Rec'd PCT/PTO 04 OCT 1993

WHAT IS CLAIMED IS:

1. A method for desulfurizing flue gases in an absorber tower while maintaining a differential pressure across the absorber inlet-outlet of zero or less; comprising:

providing an absorber tower which is devoid of packing, and having a flue gas inlet at the upper end thereof and a treated flue gas outlet toward the bottom end; and spraying into an upper region of said tower, at a position between said flue gas inlet and flue gas outlet, an aqueous slurry which includes (1) an absorbent for the sulfur-containing gases in said flue gases, and (2) one or more additional compositions which enhance the absorption of said sulfur-containing gases by scrubbing with said slurry; said sprayed slurry thereby mixing with said flue gases and descending concurrently in said tower; said tower being open and of substantially constant cross-section between the said spraying position and said flue gas outlet, with said sprayed slurry being of sufficient velocity to accelerate the gas through the absorber tower to achieve and maintain said differential pressure across the absorber from said flue gas inlet to said flue gas outlet of zero or less whereby additional flue gases are drawn into said absorber tower; and separating the treated gases from said slurry and flowing said treated gases to said outlet of said tower, wherein said absorber tower includes a sump at the bottom thereof, which defines a reservoir for said slurry, said absorber tower further being associated with pump means whereby said slurry is pumped to the upper region of said tower for spraying, and is collected at said sump following its descent in said tower.

PCT/US92/05600
03 Rec'd PCT/PTO 04 OCT 1993

2. A method in accordance with claim 1, wherein said absorbent comprises lime or limestone.

3. A method in accordance with claim 2, wherein said composition for enhancing adsorption of said sulfur-containing gases, is selected from one or more members of the group consisting of formic, adipic, glutaric, succinic acids or their salts, and the oxides, hydroxides, carbonates or sulfates of sodium or magnesium.

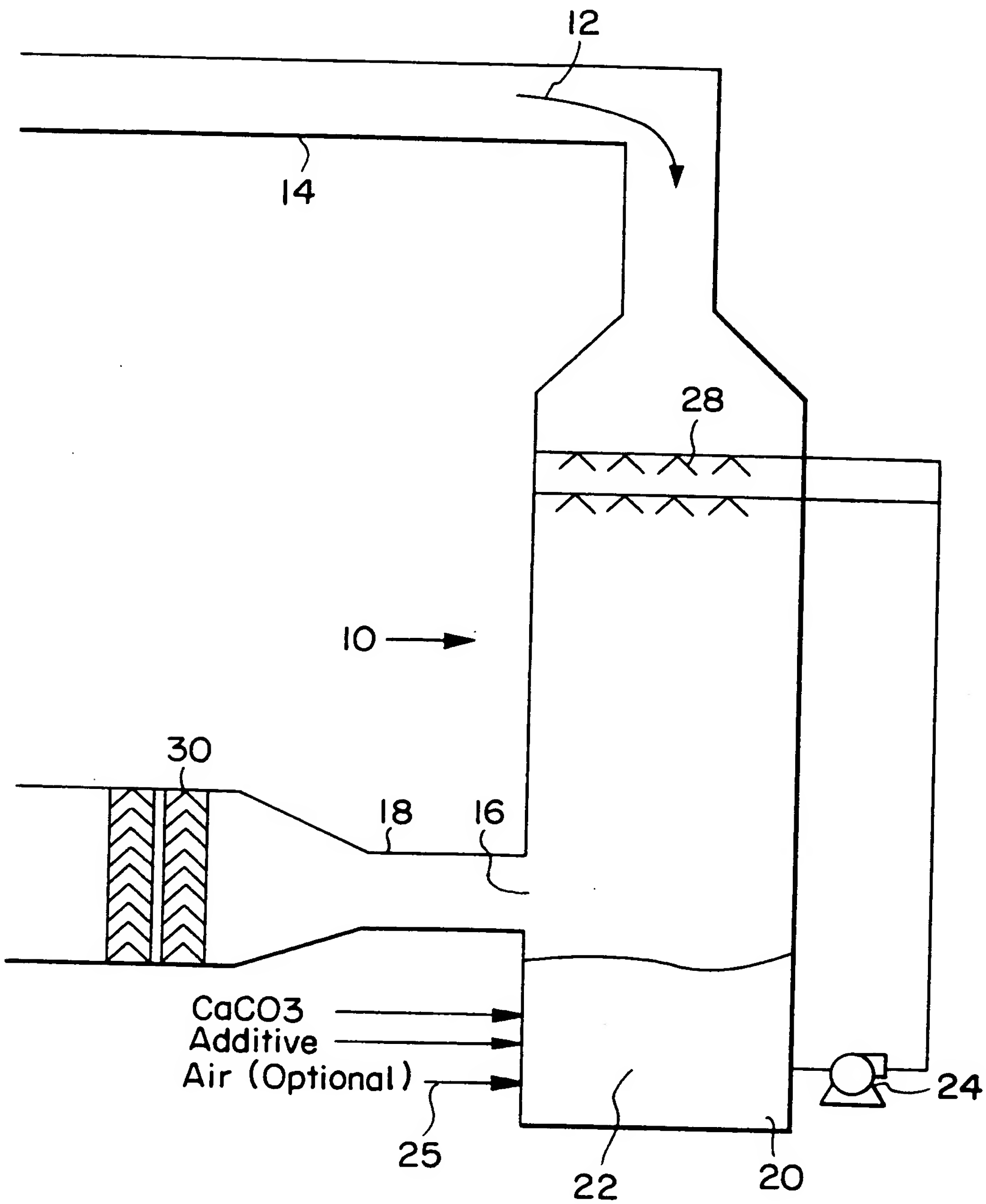
4. A method in accordance with claim 3, wherein said absorbing enhancement composition comprises a mixture of adipic, glutaric and succinic acids.

5. A method in accordance with claim 1, wherein said enhancement composition is added to said slurry at said sump.

6. A method in accordance with claim 1, further including providing forced oxidation at said sump by bubbling air into same.

7. A method in accordance with claim 1, wherein the separated treated flue gases are passed from said tower outlet to a demister.

FIG. 1



PCT/US 92/05600
IPEA/US 01 FEB 1993

FIG. 2

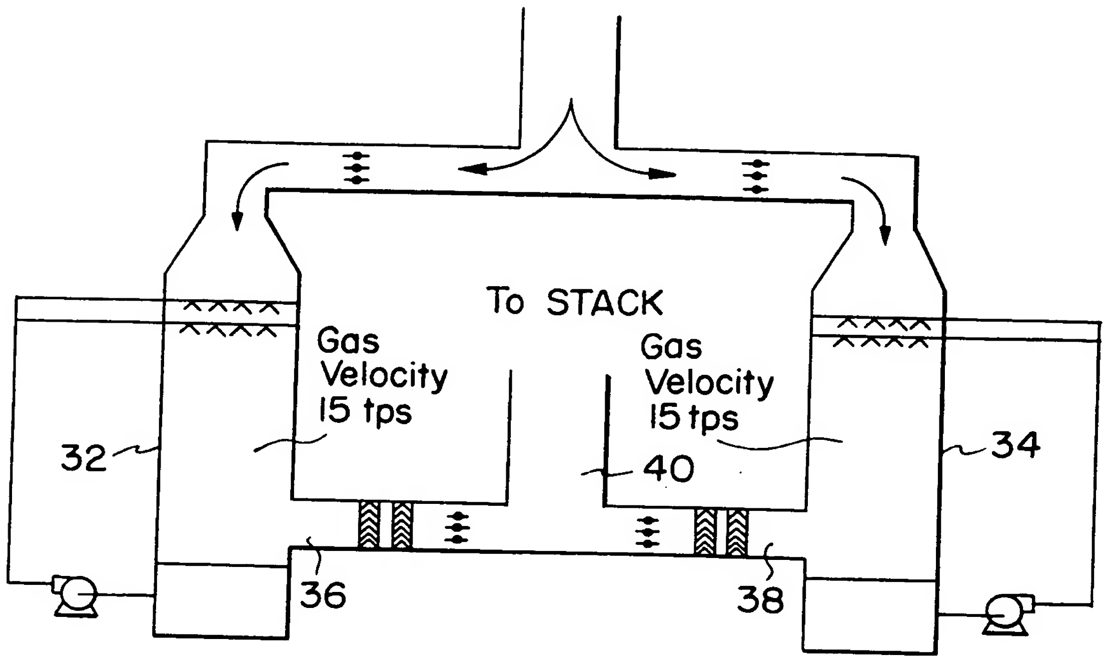


FIG. 3